```
FILE 'HOME' ENTERED AT 15:46:14 ON 16 MAY 2005

=>
Uploading
THIS COMMAND NOT AVAILABLE IN THE CURRENT FILE
Do you want to switch to the Registry File?
Choice (Y/n):
Switching to the Registry File...
Some commands only work in certain files.  For example, the EXPAND
command can only be used to look at the index in a file which has an
index.  Enter "HELP COMMANDS" at an arrow prompt (=>) for a list of
commands which can be used in this file.

=> FILE REGISTRY

COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                       0.21       0.21

FILE 'REGISTRY' ENTERED AT 15:46:28 ON 16 MAY 2005
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2005 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file
provided by InfoChem.

STRUCTURE FILE UPDATES:   15 MAY 2005  HIGHEST RN 850445-20-4
DICTIONARY FILE UPDATES:  15 MAY 2005  HIGHEST RN 850445-20-4

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

  Please note that search-term pricing does apply when
  conducting SmartSELECT searches.

*************************************************************************
*                                                                       *
* The CA roles and document type information have been removed from     *
* the IDE default display format and the ED field has been added,       *
* effective March 20, 2005.  A new display format, IDERL, is now        *
* available and contains the CA role and document type information.     *
*                                                                       *
*************************************************************************

Crossover limits have been increased.  See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more
information enter HELP PROP at an arrow prompt in the file or refer
to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=>
Uploading C:\Program Files\Stnexp\Queries\10791278b.str
```

Connecting via Winsock to STN

Welcome to STN International! Enter x:x

LOGINID:sssptasel1626

PASSWORD:
TERMINAL (ENTER 1, 2, 3, OR ?):2

* * * * * * * * * * Welcome to STN International * * * * * * * * * *

| | | | |
|---|---|---|---|
| NEWS | 1 | | Web Page URLs for STN Seminar Schedule - N. America |
| NEWS | 2 | | "Ask CAS" for self-help around the clock |
| NEWS | 3 | FEB 25 | CA/CAPLUS - Russian Agency for Patents and Trademarks (ROSPATENT) added to list of core patent offices covered |
| NEWS | 4 | FEB 28 | PATDPAFULL - New display fields provide for legal status data from INPADOC |
| NEWS | 5 | FEB 28 | BABS - Current-awareness alerts (SDIs) available |
| NEWS | 6 | FEB 28 | MEDLINE/LMEDLINE reloaded |
| NEWS | 7 | MAR 02 | GBFULL: New full-text patent database on STN |
| NEWS | 8 | MAR 03 | REGISTRY/ZREGISTRY - Sequence annotations enhanced |
| NEWS | 9 | MAR 03 | MEDLINE file segment of TOXCENTER reloaded |
| NEWS | 10 | MAR 22 | KOREAPAT now updated monthly; patent information enhanced |
| NEWS | 11 | MAR 22 | Original IDE display format returns to REGISTRY/ZREGISTRY |
| NEWS | 12 | MAR 22 | PATDPASPC - New patent database available |
| NEWS | 13 | MAR 22 | REGISTRY/ZREGISTRY enhanced with experimental property tags |
| NEWS | 14 | APR 04 | EPFULL enhanced with additional patent information and new fields |
| NEWS | 15 | APR 04 | EMBASE - Database reloaded and enhanced |
| NEWS | 16 | APR 18 | New CAS Information Use Policies available online |
| NEWS | 17 | APR 25 | Patent searching, including current-awareness alerts (SDIs), based on application date in CA/CAplus and USPATFULL/USPAT2 may be affected by a change in filing date for U.S. applications. |
| NEWS | 18 | APR 28 | Improved searching of U.S. Patent Classifications for U.S. patent records in CA/CAplus |

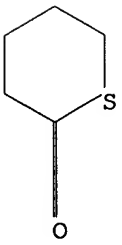
NEWS EXPRESS JANUARY 10 CURRENT WINDOWS VERSION IS V7.01a, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 10 JANUARY 2005

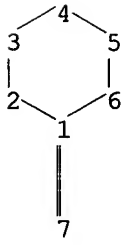
| | |
|---|---|
| NEWS HOURS | STN Operating Hours Plus Help Desk Availability |
| NEWS INTER | General Internet Information |
| NEWS LOGIN | Welcome Banner and News Items |
| NEWS PHONE | Direct Dial and Telecommunication Network Access to STN |
| NEWS WWW | CAS World Wide Web Site (general information) |

Enter NEWS followed by the item number or name to see news on that specific topic.



* * * * * * * * * * * * * * * STN Columbus * * * * * * * * * * * * * * * *



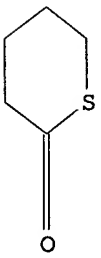




chain nodes :
7
ring nodes :
1 2 3 4 5 6
chain bonds :
1-7
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6
exact/norm bonds :
1-7
exact bonds :
1-2 1-6 2-3 3-4 4-5 5-6
isolated ring systems :
containing 1 :

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS

L1 STRUCTURE UPLOADED

=> d
L1 HAS NO ANSWERS
L1 STR




Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 15:46:38 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 210 TO ITERATE

100.0% PROCESSED 210 ITERATIONS 4 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 3331 TO 5069

PROJECTED ANSWERS: 4 TO 200

L2 4 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 15:46:42 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 4756 TO ITERATE

100.0% PROCESSED 4756 ITERATIONS 105 ANSWERS
SEARCH TIME: 00.00.01

L3 105 SEA SSS FUL L1

=> file caplus

| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION |
|---|---|---|
| FULL ESTIMATED COST | 161.33 | 161.54 |

FILE 'CAPLUS' ENTERED AT 15:46:45 ON 16 MAY 2005
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2005 AMERICAN CHEMICAL SOCIETY (ACS)



FILE COVERS 1907 - 16 May 2005 VOL 142 ISS 21
FILE LAST UPDATED: 15 May 2005 (20050515/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l3
L4 79 L3

=> file reg

| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION |
|---|---|---|
| FULL ESTIMATED COST | 0.45 | 161.99 |

FILE 'REGISTRY' ENTERED AT 15:46:55 ON 16 MAY 2005
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2005 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 15 MAY 2005 HIGHEST RN 850445-20-4
DICTIONARY FILE UPDATES: 15 MAY 2005 HIGHEST RN 850445-20-4

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

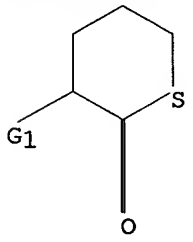
Please note that search-term pricing does apply when conducting SmartSELECT searches.

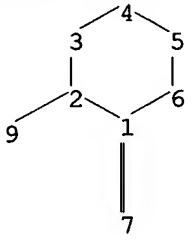
**********
* *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
* *
**********

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=>
Uploading C:\Program Files\Stnexp\Queries\10791278c.str



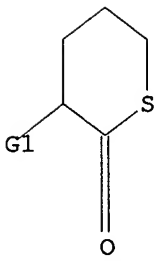

chain nodes :
7 9
ring nodes :
1 2 3 4 5 6
chain bonds :
1-7 2-9
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6
exact/norm bonds :
1-7 2-9
exact bonds :
1-2 1-6 2-3 3-4 4-5 5-6
isolated ring systems :
containing 1 :

G1:C,O,S,N

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 9:CLASS

L5 STRUCTURE UPLOADED

=> d
L5 HAS NO ANSWERS
L5 STR




G1 C,O,S,N

Structure attributes must be viewed using STN Express query preparation.

=> s l5
SAMPLE SEARCH INITIATED 15:47:48 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 89 TO ITERATE

100.0% PROCESSED 89 ITERATIONS 3 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 1214 TO 2346
PROJECTED ANSWERS: 3 TO 163

L6 3 SEA SSS SAM L5

=> s l5 full
FULL SEARCH INITIATED 15:47:51 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 2015 TO ITERATE

100.0% PROCESSED 2015 ITERATIONS 52 ANSWERS
SEARCH TIME: 00.00.01

L7 52 SEA SSS FUL L5

=> file caplus

| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION |
|---|---|---|
| FULL ESTIMATED COST | 161.76 | 323.75 |

FILE 'CAPLUS' ENTERED AT 15:47:55 ON 16 MAY 2005


FILE COVERS 1907 - 16 May 2005 VOL 142 ISS 21
FILE LAST UPDATED: 15 May 2005 (20050515/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l7
L8 25 L7

=> d ibib abs hitstr tot
THE ESTIMATED COST FOR THIS REQUEST IS 123.50 U.S. DOLLARS
DO YOU WANT TO CONTINUE WITH THIS REQUEST? (Y)/N:y

L8 ANSWER 1 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

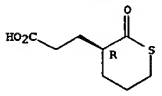
ACCESSION NUMBER: 2005:154385 CAPLUS
DOCUMENT NUMBER: 142:348878
TITLE: Enantiospecificity of Glutamate Carboxypeptidase II Inhibition
AUTHOR(S): Tsukamoto, Takashi; Majer, Pavel; Vitharana, Dilrukshi; Ni, Chiyou; Hin, Bunda; Lu, Xi-Chun M.; Thomas, Ajit G.; Wozniak, Krystyna M.; Calvin, David C.; Wu, Ying; Slusher, Barbara S.; Scarpetti, David; Bonneville, George W.
CORPORATE SOURCE: Guilford Pharmaceuticals Inc., Baltimore, MD, 21224, USA
SOURCE: Journal of Medicinal Chemistry (2005), 48(7), 2319-2324
CODEN: JMCMAR; ISSN: 0022-2623
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Two representative glutamate carboxypeptidase II (GCP II) inhibitors, 2-(hydroxypentafluorophenylmethyl-phosphinoylmethyl)pentanedioic acid 2 and 2-(3-mercaptopropyl)pentanedioic acid 3, were synthesized in high optical purities (>97%ee). The two enantiomers of 2 were prepared from previously reported chiral intermediates, (R)- and (S)-2-(hydroxyphosphinoylmethyl)pentanedioic acid benzyl esters 8. The synthesis of (R)- and (S)-3 involves the hydrolysis of (R)- and (S)-3-(2-oxo-tetrahydro-thiopyran-3-yl)propionic acids, (R)- and (S)-11, the corresponding optically pure thiolactones delivered by chiral chromatog. separation of the racemic 11. GCP II inhibitory assay revealed that (S)-2 is 40-fold more potent than (R)-2. In contrast, both enantiomers of 3 inhibited GCP II with nearly equal potency. The efficacy observed in subsequent animal studies with these enantiomers correlated well with the inhibitory potency in a GCP II assay.

IT **848952-59-0P 848952-60-3P**
RL: PRP (Properties); PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(glutamate carboxypeptidase II inhibitors preparation and enantiospecific activity)

RN 848952-59-0 CAPLUS
CN 2H-Thiopyran-3-propanoic acid, tetrahydro-2-oxo-, (3R)- (9CI) (CA INDEX NAME)

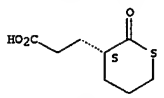
Absolute stereochemistry.



RN 848952-60-3 CAPLUS
CN 2H-Thiopyran-3-propanoic acid, tetrahydro-2-oxo-, (3S)- (9CI) (CA INDEX NAME)

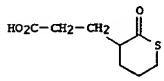
Absolute stereochemistry.

L8 ANSWER 1 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)



IT **757246-49-4P**
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(glutamate carboxypeptidase II inhibitors preparation and enantiospecific activity)

RN 757246-49-4 CAPLUS
CN 2H-Thiopyran-3-propanoic acid, tetrahydro-2-oxo- (9CI) (CA INDEX NAME)



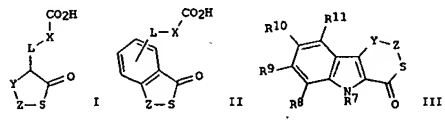
REFERENCE COUNT: 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2004:756706 CAPLUS
DOCUMENT NUMBER: 141:277490
TITLE: Preparation of thiolactone derivatives as inhibitors of NAALADase enzyme
INVENTOR(S): Tsukamoto, Takashi; Slusher, Barbara S.
PATENT ASSIGNEE(S): Guilford Pharmaceuticals Inc., USA
SOURCE: PCT Int. Appl., 69 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | | DATE |
|---|---|---|---|---|---|
| WO 2004078742 | A1 | 20040916 | WO 2004-US6178 | | 20040303 |
| W: AE, AE, AG, AL, AL, AM, AM, AM, AT, AT, AU, AZ, AZ, BA, BB, BG, BG, BR, BR, BW, BY, BY, BZ, BZ, CA, CH, CN, CN, CO, CO, CR, CR, CU, CU, CZ, CZ, DE, DE, DK, DK, DM, DZ, EC, EC, EE, EE, EG, ES, ES, FI, FI, GB, GD, GE, GE, GH, GM, HR, HR, HU, HU, ID, IL, IN, IS, JP, JP, KE, KE, KG, KG, KP, KP, KP, KR, KR, KZ, KZ, KZ, LC, LK, LR, LS, LS, LT, LU, LV, MA, MD, MD, MG, MK, MN, MW, MX, MX, MZ, MZ, NA, NI | | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | | |
| US 2005004203 | A1 | 20050106 | US 2004-791278 | | 20040303 |
| PRIORITY APPLN. INFO.: | | | US 2003-450648P | P | 20030303 |
| OTHER SOURCE(S): | | MARPAT 141:277490 | | | |

GI



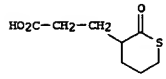
AB Title compds. represented by the formula I, II and III [wherein X = (un)substituted (cyclo)alkylene, (cyclo)alkenylene, alkynylene, (hetero)aryl; L = a bond, CR1R2, O, S, SO2, NR1; Y = O, S, CR3R4, NR3; Z = (CR5R6)n; n = 1-4; R1-R6 = independently H, (un)substituted alkyl, alkenyl; R7 = H, (un)substituted Ph, phenylethyl, benzyl; R8-R11 = independently H, carboxy, hydroxy, halo, nitro, cyano, alkyl, alkoxy; and pharmaceutically acceptable equivalent, an optical isomer or a mixture of isomers thereof] were prepared as NAALADase enzyme inhibitors. For example, cyclization of 2-[3-(tritylthio)mercaptopropyl]pentanedioic acid in acidic condition gave 3-(2-oxotetrahydrothiopyran-3-yl)propionic acid (IV) in 37% yield. 2-(3-Sulfanylpropyl)pentanedioic acid was tested for inhibition of NAALADase enzyme activity in treatment of retinal disorders, and IV was tested for protective effect of NAALADase inhibitors in exptl. rat glaucoma. Thus, this invention provided new compds., pharmaceutical compns. and diagnostic kits comprising such compds., and methods of using

L8 ANSWER 2 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

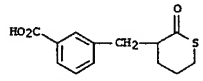
such compds. for inhibiting NAALADase enzyme activity, detecting diseases where NAALADase levels are altered, inhibiting angiogenesis, effecting a TGF-β activity or a neuronal activity, and treating a glutamate abnormality, a compulsive disorder, neuropathy, pain, a prostate disease, cancer, Huntington's disease, diabetes, a retinal disorder or glaucoma.

IT **757246-49-4P 757246-50-7P**
RL: PAC (Pharmacological activity); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(preparation of thiolactones as inhibitors of NAALADase enzyme)

RN 757246-49-4 CAPLUS
CN 2H-Thiopyran-3-propanoic acid, tetrahydro-2-oxo- (9CI) (CA INDEX NAME)



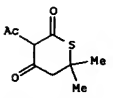
RN 757246-50-7 CAPLUS
CN Benzoic acid, 3-[(tetrahydro-2-oxo-2H-thiopyran-3-yl)methyl]- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

Instant App

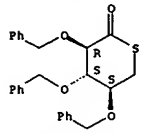
L8 ANSWER 3 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2003:608863 CAPLUS
DOCUMENT NUMBER: 140:27736
TITLE: Synthesis of enol methyl ethers of 3-acetyl-6,6-dimethyltetrahydrothiopyran-2,4-dione and their reactions with amines
AUTHOR(S): Zheldakova, T. A.; Budnikova, M. V.; Rubinov, D. B.
CORPORATE SOURCE: Institute of Bioorganic Chemistry, Belarussian Academy of Sciences, Minsk, 220141, Belarus
SOURCE: Russian Journal of Organic Chemistry (Translation of Zhurnal Organicheskoi Khimii) (2003), 39(2), 235-241
CODEN: RJOCEQ; ISSN: 1070-4280
PUBLISHER: MAIK Nauka/Interperiodica Publishing
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 140:27736
AB The reaction of 3-acetyl-6,6-dimethyltetrahydrothiopyran-2,4-dione with diazomethane furnishes a mixture of 3-acetyl-6,6-dimethyl-4-methoxy-5,6-dihydro-2H-thiopyran-2-one and 3-acetyl-6,6-dimethyl-2-methoxy-5,6-dihydro-2H-thiopyran-4-one in 2:3 ratio, whereas in reaction with di-Me sulfate in the presence of potassium carbonate forms a mixture of the same products in 9:1 ratio. In both reactions the overall yield of ethers amts. to 50%. Treating of regioisomeric enol Me ethers with pyrrolidine, o-toluidine, and allylamine provides the corresponding endocyclic enaminodiketones.
IT 359888-70-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of enol Me ethers of acetyldimethyltetrahydrothiopyrandione and their reactions with amines)
RN 359888-70-3 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-acetyldihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 4 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2003:421647 CAPLUS
DOCUMENT NUMBER: 139:261463
TITLE: New 1-C-(5-thio-D-xylopyranosyl) derivatives as potential orally active venous antithrombotics
AUTHOR(S): Mignon, Laurent; Goichot, Christophe; Ratel, Philippe; Cagnin, Gerald; Baudry, Michel; Praly, Jean-Pierre; Boubia, Benaissa; Barberousse, Veronique
CORPORATE SOURCE: Laboratoires Fournier, Daix, 21121, Fr.
SOURCE: Carbohydrate Research (2003), 338(12), 1271-1282
CODEN: CRBRAT; ISSN: 0008-6215
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 139:261463
AB In the search for new orally active antithrombotic drugs that are metabolically stable, we explored the synthesis of 1-C-(5-thio-D-xylosyl) derivs., examining radical and nucleophilic methods. Thus synthesized were aryl, benzyl, alkylcarboxymethylenyl, arylsulfonylmethylenyl and alkylaminocarboxymethylenyl C-linked analogs of 5-thio-D-xylopyranosides.
IT 601495-28-7P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of aryl, benzyl, alkylcarboxymethylenyl, arylsulfonylmethylenyl and alkylaminocarboxymethylenyl 1-C-(5-thio-D-xylopyranosyl) derivs. to be tested as potential orally active venous antithrombotics)
RN 601495-28-7 CAPLUS
CN D-Xylonic acid, 2,3,4-tris-O-(phenylmethyl)-5-thio-, δ-thiolactone (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



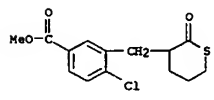
REFERENCE COUNT: 49 THERE ARE 49 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 5 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2002:555453 CAPLUS
DOCUMENT NUMBER: 137:124986
TITLE: Preparation of thiol-based NAALADase inhibitors and their uses thereof
INVENTOR(S): Tsukamoto, Takashi; Majer, Pavel; Stoermer, Doris; Slusher, Barbara S.
PATENT ASSIGNEE(S): Guilford Pharmaceuticals Inc., USA
SOURCE: PCT Int. Appl., 202 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| WO 2002057222 | A2 | 20020725 | WO 2002-US1205 | 20020117 |
| WO 2002057222 | A3 | 20021219 | | |
| WO 2002057222 | C2 | 20040506 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| CA 2435273 | AA | 20020725 | CA 2002-2435273 | 20020117 |
| US 2003105088 | A1 | 20030605 | US 2002-46917 | 20020117 |
| US 6586623 | B2 | 20030701 | | |
| EP 1353903 | A2 | 20031022 | EP 2002-713419 | 20020117 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| JP 2004524294 | T2 | 20040812 | JP 2002-557903 | 20020117 |
| US 2003216468 | A1 | 20031120 | US 2003-431462 | 20030508 |
| US 6812364 | B2 | 20041102 | | |
| US 2005085503 | A1 | 20050421 | US 2004-959199 | 20041007 |
| PRIORITY APPLN. INFO.: | | | US 2001-261754P | P 20010117 |
| | | | US 2001-342772P | P 20011228 |
| | | | US 2002-46917 | A3 20020117 |
| | | | WO 2002-US1205 | W 20020117 |
| | | | US 2003-431462 | A3 20030508 |

OTHER SOURCE(S): MARPAT 137:124986
AB This invention relates to new compds., pharmaceutical compns. and diagnostic kits comprising such compds., and methods of using such compds. for inhibiting NAALADase enzyme activity, detecting diseases where NAALADase levels are altered, effecting neuronal activity, effecting TGF-b activity, inhibiting angiogenesis, and treating glutamate abnormalities, diabetic neuropathy, pain, compulsive disorders, prostate diseases, cancers and glaucoma. Thus, rats treated with NAALADase inhibitor 3-carboxy-5-(1,1-dimethylethyl)-alpha-(3-mercaptopropyl)benzenepropanoic acid of this invention at various dose levels (10, 1, 0.1 mg/kg) for 15 days after sciatic nerve ligation showed normalized difference in scores between the operated and unoperated paws compared to continued hyperalgesic for rats treated with vehicle under the same conditions.
IT 377731-27-6P
RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)

L8 ANSWER 5 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
(in prepn. and uses of thiol-based NAALADase inhibitors)
RN 377731-27-6 CAPLUS
CN Benzoic acid, 4-chloro-3-[(tetrahydro-2-oxo-2H-thiopyran-3-yl)methyl]-, methyl ester (9CI) (CA INDEX NAME)



L8 ANSWER 6 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2002:521373 CAPLUS
DOCUMENT NUMBER: 137:93151
TITLE: Autoinducer lactones, furanones and signal peptides and their uses as performance-enhancing feed additives.
INVENTOR(S): Jonker, Jan
PATENT ASSIGNEE(S): Gormar Marketing Limited, Cayman I.
SOURCE: PCT Int. Appl., 38 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | | DATE |
|---|---|---|---|---|---|
| WO 2002052949 | A1 | 20020711 | WO 2002-GB72 | | 20020108 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM | | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | | |
| CA 2434117 | AA | 20020711 | CA 2002-2434117 | | 20020108 |
| EP 1361801 | A1 | 20031119 | EP 2002-727000 | | 20020108 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | | |
| JP 2004525617 | T2 | 20040826 | JP 2002-553913 | | 20020108 |
| US 2004115245 | A1 | 20040617 | US 2004-250842 | | 20040114 |
| PRIORITY APPLN. INFO.: | | | GB 2001-387 | A | 20010108 |
| | | | GB 2001-9477 | A | 20010418 |
| | | | WO 2002-GB72 | W | 20020108 |

OTHER SOURCE(S): MARPAT 137:93151

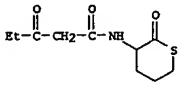
AB The present invention discloses the autoinducer compds., such as acyl homoserine lactones, acyl homocysteine lactone, acyl thiolactones, furanones or signal peptides, and their use in animal feed additives and animal feeds to improve animal performance.

IT **441350-81-8 441350-82-9 441350-83-0**
**441350-84-1 441350-85-2 441350-86-3**
**441350-87-4 441350-88-5 441350-89-6**
**441350-90-9 441350-91-0 441350-92-1**
**441350-93-2 441350-94-3**
RL: FFD (Food or feed use); BIOL (Biological study); USES (Uses)
(autoinducer lactones, furanones and signal peptides and their uses as performance-enhancing feed additives)

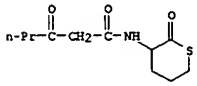
RN 441350-81-8 CAPLUS
CN Butanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



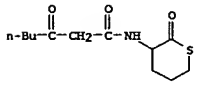
RN 441350-82-9 CAPLUS
CN Pentanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



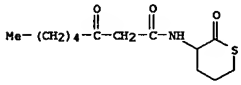
RN 441350-83-0 CAPLUS
CN Hexanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



RN 441350-84-1 CAPLUS
CN Heptanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

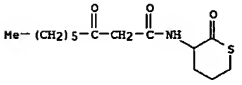


RN 441350-85-2 CAPLUS
CN Octanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

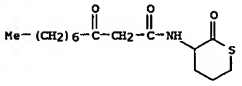




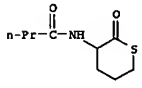
RN 441350-86-3 CAPLUS
CN Nonanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



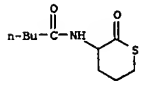
RN 441350-87-4 CAPLUS
CN Decanamide, 3-oxo-N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



RN 441350-88-5 CAPLUS
CN Butanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

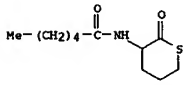


RN 441350-89-6 CAPLUS
CN Pentanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

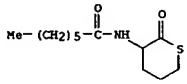


RN 441350-90-9 CAPLUS
CN Hexanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

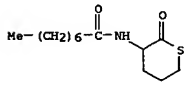




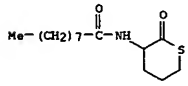
RN 441350-91-0 CAPLUS
CN Heptanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



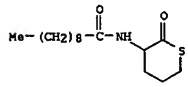
RN 441350-92-1 CAPLUS
CN Octanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



RN 441350-93-2 CAPLUS
CN Nonanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



RN 441350-94-3 CAPLUS
CN Decanamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 6 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

L8 ANSWER 7 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2001:886142 CAPLUS
DOCUMENT NUMBER: 136:15255
TITLE: NAALADase inhibitors for treating retinal disorders and glaucoma
INVENTOR(S): Slusher, Barbara S.; Wozniak, Krystyna
PATENT ASSIGNEE(S): Guilford Pharmaceuticals Inc., USA
SOURCE: PCT Int. Appl., 196 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| WO 2001092274 | A2 | 20011206 | WO 2001-US17288 | 20010530 |
| WO 2001092274 | A3 | 20020530 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG | | | | |
| CA 2410889 | AA | 20011206 | CA 2001-2410889 | 20010530 |
| US 2003036534 | A1 | 20030220 | US 2001-866961 | 20010530 |
| EP 1292601 | A2 | 20030319 | EP 2001-944182 | 20010530 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| JP 2003535098 | T2 | 20031125 | JP 2002-500887 | 20010530 |
| PRIORITY APPLN. INFO.: | | | US 2000-207320P | P 20000530 |
| | | | WO 2001-US17288 | W 20010530 |

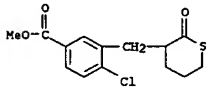
OTHER SOURCE(S): MARPAT 136:15255

AB The invention discloses pharmaceutical compns. and methods for treating a retinal disorder or glaucoma using NAALADase inhibitors.

IT **377731-27-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction; NAALADase inhibitors for treating retinal disorders and glaucoma)

RN 377731-27-6 CAPLUS

CN Benzoic acid, 4-chloro-3-[(tetrahydro-2-oxo-2H-thiopyran-3-yl)methyl]-, methyl ester (9CI) (CA INDEX NAME)



L8 ANSWER 8 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2001:885736 CAPLUS
DOCUMENT NUMBER: 136:15243
TITLE: NAALADase inhibitors for treating amyotrophic lateral sclerosis
INVENTOR(S): Slusher, Barbara S.; Wozniak, Krystyna
PATENT ASSIGNEE(S): Guilford Pharmaceuticals Inc., USA
SOURCE: PCT Int. Appl., 79 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| WO 2001091738 | A2 | 20011206 | WO 2001-US17325 | 20010530 |
| WO 2001091738 | A3 | 20020906 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG | | | | |
| US 2002013295 | A1 | 20020131 | US 2001-866729 | 20010530 |
| PRIORITY APPLN. INFO.: | | | US 2000-207319P | P 20000530 |

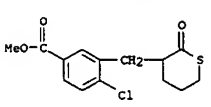
OTHER SOURCE(S): MARPAT 136:15243

AB The invention discloses pharmaceutical compns. and methods for treating amyotrophic lateral sclerosis using NAALADase inhibitors.

IT **377731-27-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction; NAALADase inhibitors for treating amyotrophic lateral sclerosis)

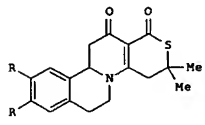
RN 377731-27-6 CAPLUS

CN Benzoic acid, 4-chloro-3-[(tetrahydro-2-oxo-2H-thiopyran-3-yl)methyl]-, methyl ester (9CI) (CA INDEX NAME)

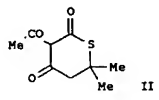


L8 ANSWER 9 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 2001:482856 CAPLUS
DOCUMENT NUMBER: 135:242389
TITLE: New N,S-diheteroatomic steroid analogs. Annelation of 3,4-dihydroisoquinolines by 3-acetylthiopyran-2,4-dione
AUTHOR(S): Budnikova, M. V.; Zheldakova, T. A.; Rubinov, D. B.; Mikhal'chuk, A. L.
CORPORATE SOURCE: Institute of Bioorganic Chemistry, Belarussian Academy of Sciences, Minsk, 220141, Belarus
SOURCE: Russian Journal of Organic Chemistry (Translation of Zhurnal Organicheskoi Khimii) (2001), 37(2), 293-294
CODEN: RJOCEQ; ISSN: 1070-4280
PUBLISHER: MAIK Nauka/Interperiodica Publishing
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:242389
GI



I



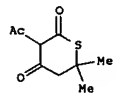
II

AB Syntheses of azathiasteroids I (R = H, OMe) in 54.5 and 65% yields, resp., were achieved via a cyclocondensation reaction of the thiopyran-2,4-dione II with 3,4-dihydroisoquinoline or 6,7-dimethoxy-3,4-dihydroisoquinoline by refluxing for 24 h in EtOH.

IT **359888-70-3**
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of azathiasteroid analogs via cyclization of 3,4-dihydroisoquinolines with 3-acetylthiopyran-2,4-dione)

RN 359888-70-3 CAPLUS

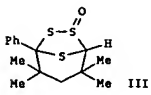
CN 2H-Thiopyran-2,4(3H)-dione, 3-acetyldihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



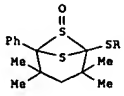
REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 10 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

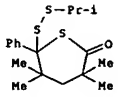
ACCESSION NUMBER: 1999:548678 CAPLUS
DOCUMENT NUMBER: 131:299188
TITLE: Rearrangement of the carbanion generated from a tied-back 1,2,4-trithiolane oxide (6,7,8-trithiabicyclo[3.2.1]octane 6-oxide)
AUTHOR(S): Ishii, Akihiko; Nakaniwa, Tetsuya; Umezawa, Kazuyo; Nakayama, Juzo
CORPORATE SOURCE: Department of Chemistry, Faculty of Science, Saitama University, Saitama, 338-8570, Japan
SOURCE: Tetrahedron (1999), 55(34), 10341-10350
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



III



XII

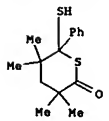


XIV

AB Treatment of 2,2,4,4-tetramethyl-6,7,8-trithiabicyclo[3.2.1]octane 6-exo-oxide (III) with LDA, followed by treatment with D2O, RI (R = Me, Et), and 2-PrBr, yielded the bridgehead-deuterated starting compound, bicyclic 1,3-dithietane oxides (XII), and (2-propyldithio)thiolactone (XIV), resp. The initially-formed bridgehead lithium salt opens the bicyclic skeleton to give the lithium δ-thioxoperoxydithiocarboxylate, which finally isomerizes to the lithium (3-oxo-2-thianyl)disulfide via the peroxydithiocarboxylate-α-oxodisulfide rearrangement.

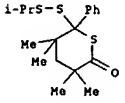
IT **247090-31-9P**
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (crystallog.; rearrangement mechanism of the carbanion generated from a tied-back 1,2,4-trithiolane oxide (6,7,8-trithiabicyclo[3.2.1]octane 6-oxide))
RN 247090-31-9 CAPLUS
CN 2H-Thiopyran-2-one, tetrahydro-3,3,5,5-tetramethyl-6-[(1-methylethyl)dithio]-6-phenyl- (9CI) (CA INDEX NAME)

L8 ANSWER 10 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)



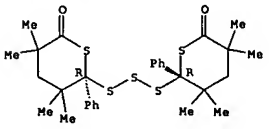
REFERENCE COUNT: 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 10 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)



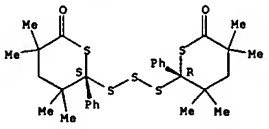
IT **247090-32-0P 247090-33-1P 247090-34-2P**
RL: SPN (Synthetic preparation); PREP (Preparation) (rearrangement mechanism of the carbanion generated from a tied-back 1,2,4-trithiolane oxide (6,7,8-trithiabicyclo[3.2.1]octane 6-oxide))
RN 247090-32-0 CAPLUS
CN 2H-Thiopyran-2-one, 6,6'-trithiobis[tetrahydro-3,3,5,5-tetramethyl-6-phenyl-, (6R,6'R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 247090-33-1 CAPLUS
CN 2H-Thiopyran-2-one, 6,6'-trithiobis[tetrahydro-3,3,5,5-tetramethyl-6-phenyl-, (6R,6'S)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



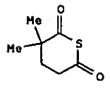
RN 247090-34-2 CAPLUS
CN 2H-Thiopyran-2-one, tetrahydro-6-mercapto-3,3,5,5-tetramethyl-6-phenyl- (9CI) (CA INDEX NAME)

L8 ANSWER 11 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1995:658527 CAPLUS
DOCUMENT NUMBER: 123:227968
TITLE: Synthesis of small-medium ring thioanhydrides
AUTHOR(S): Kates, Michael J.; Schauble, J. Herman
CORPORATE SOURCE: Department of Chemistry, Villanova University, Villanova, PA, 19085, USA
SOURCE: Journal of Heterocyclic Chemistry (1995), 32(3), 971-8
CODEN: JHTCAD; ISSN: 0022-152X
PUBLISHER: HeteroCorporation
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 123:227968

AB Reaction of five-membered ring anhydrides with sodium sulfide has previously been employed for synthesis of the corresponding thioanhydrides in low yields. Reexamn. of the stoichiometry reveals reaction of cyclic anhydride with sodium sulfide (2:1 resp.), affords the thioanhydride accompanied by the corresponding dicarboxylate in a 1:1 molar ratio. The mechanistic pathway for this reaction has also been elucidated. Optimization of reaction conditions has resulted in the synthesis of a variety of four to seven-membered ring thioanhydrides in yields approaching theor. The reaction of disodium sulfide with 1,1-cyclobutanedicarboxylic acid gave 2-thiaspiro[3.3]heptane-1,3-dione (74% yield). The reaction of 1,2-benzenedicarboxylic acid gave benzo[c]thiophene-1,3-dione.

IT **168280-83-9P**
RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of small or medium-sized sulfur-containing heterocyclic compds.)
RN 168280-83-9 CAPLUS
CN 2H-Thiopyran-2,6(3H)-dione, dihydro-3,3-dimethyl- (9CI) (CA INDEX NAME)



L8 ANSWER 12 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1995:275031 CAPLUS
DOCUMENT NUMBER: 122:74619
TITLE: Pesticide for preventing and eliminating pests with high pesticide resistance
INVENTOR(S): Liu, Runxi
PATENT ASSIGNEE(S): Peop. Rep. China
SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 18 pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

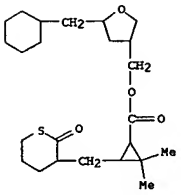
| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| CN 1081063 | A | 19940126 | CN 1992-105309 | 19920706 |

PRIORITY APPLN. INFO.: CN 1992-105309 19920706

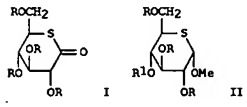
AB The pesticide is prepared from oxime group-containing bactericides 3-10 weight%, heterocyclic pyrethrin 10-20, F-containing or heterocyclic pyrethrin 3-5, diesel oil 30-36, first emulsifier 4-5, second emulsifier 4-5, solvent 9-36., and enhanced P SV1 10.

IT **160219-71-6**, Saienjuzhi
RL: AGR (Agricultural use); BIOL (Biological study); USES (Uses)
(pesticide for preventing and eliminating pests with high pesticide resistance)

RN 160219-71-6 CAPLUS
CN Cyclopropanecarboxylic acid, 2,2-dimethyl-3-[(tetrahydro-2-oxo-2H-thiopyran-3-yl)methyl]-, [5-(cyclohexylmethyl)tetrahydro-3-furanyl]methyl ester (9CI) (CA INDEX NAME)



L8 ANSWER 13 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1991:62536 CAPLUS
DOCUMENT NUMBER: 114:62536
TITLE: Synthesis of per-O-alkylated 5-thio-D-glucono-1,5-lactones and transannular participation of the ring sulfur atom of 5-thio-D-glucose derivatives on solvolysis under acidic conditions
AUTHOR(S): Yuasa, Hideya; Tamura, Junichi; Hashimoto, Hironobu
CORPORATE SOURCE: Tokyo Inst. Technol., Fac. Sci., Yokohama, 227, Japan
SOURCE: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1990), (10), 2763-9
CODEN: JCPRB4; ISSN: 0300-922X
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 114:62536
GI

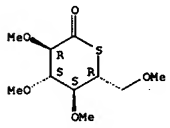


AB Thiogluconolactones I (R = Me, CH2PH, CH2CH:CH2) were synthesized via acetolysis or hydrolysis of the corresponding Me glucosides II (R = R1 = same) (III). Transannular participation of the S atom on acid methanolysis of 3,6-di-O-5-S-acetyl-1,2-O-isopropylidene-5-thio-α-D-glucofuranose and on acetolysis of the glycosides III was confirmed. These reactions gave unexpected 4-substituted derivs. II (R = Me, CH2CH:CH2, R1 = Ac, Me). Furthermore, similar participation on C-2 and C-6 was suggested from the formation of 2,5-dideoxy-2,5-epithio-4,6-di-O-methyl-D-mannose di-Me acetal.

IT **131757-90-9P 131757-91-0P 131757-92-1P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 131757-90-9 CAPLUS
CN D-Gluconic acid, 2,3,4,6-tetra-O-methyl-5-thio-, δ-thiolactone (9CI) (CA INDEX NAME)

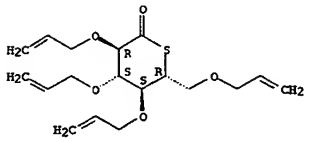
Absolute stereochemistry.



RN 131757-91-0 CAPLUS
CN D-Gluconic acid, 2,3,4,6-tetra-O-2-propenyl-5-thio-, δ-thiolactone (9CI) (CA INDEX NAME)

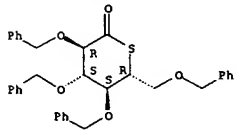
L8 ANSWER 13 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

Absolute stereochemistry.



RN 131757-92-1 CAPLUS
CN D-Gluconic acid, 2,3,4,6-tetrakis-O-(phenylmethyl)-5-thio-, δ-thiolactone (9CI) (CA INDEX NAME)

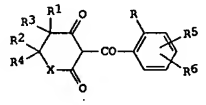
Absolute stereochemistry.



L8 ANSWER 14 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1988:204499 CAPLUS
DOCUMENT NUMBER: 108:204499
TITLE: Preparation and formulation of 4-oxo-3-benzoylvalerolactones and thiolactones as herbicides
INVENTOR(S): Knudsen, Christopher Glade; Michaely, William James; James, Donald Richard; Chin, Hsiao Ling Mao
PATENT ASSIGNEE(S): Stauffer Chemical Co., USA
SOURCE: Eur. Pat. Appl., 30 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| EP 249812 | A2 | 19871223 | EP 1987-108078 | 19870604 |
| EP 249812 | A3 | 19890125 | | |
| R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, NL | | | | |
| US 4741755 | A | 19880503 | US 1986-871975 | 19860609 |
| AU 8773882 | A1 | 19871210 | AU 1987-73882 | 19870605 |
| AU 590421 | B2 | 19891102 | | |
| HU 43923 | A2 | 19880128 | HU 1987-2608 | 19870608 |
| ZA 8704097 | A | 19880330 | ZA 1987-4097 | 19870608 |
| JP 62298585 | A2 | 19871225 | JP 1987-142407 | 19870609 |
| CN 87104116 | A | 19880120 | CN 1987-104116 | 19870609 |
| BR 8702908 | A | 19880308 | BR 1987-2908 | 19870609 |
| US 4780123 | A | 19881025 | US 1987-135208 | 19871221 |
| US 4780124 | A | 19881025 | US 1987-135892 | 19871221 |
| US 4808733 | A | 19890228 | US 1987-135216 | 19871221 |

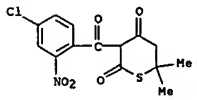
PRIORITY APPLN. INFO.: US 1986-871975 A 19860609
OTHER SOURCE(S): CASREACT 108:204499
GI



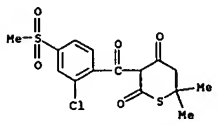
AB The title compds. I ( R = halo, C1-2 alkyl, C1-2 alkoxy, NO2, cyano, C1-2 haloalkyl, RaSOn, ; Ra = C1-2 alkyl; R1, R2, R3, R4 = H, C1-4 alkyl; R3R4 = bond; R1R3, R2R4 = C2-5 alkylene; R5, R6 = H, halo, C1-4 alkyl, C1-4 alkoxy, F3CO, cyano, NO2, C1-4 haloalkyl, etc.; X = O, S; n = 0-2) and their salts were prepared 6-Methyl-4-oxovalerolactone and 2-(O2N)C6H4COCl were stirred at room temp in CH2Cl2 containing Et3N to give the enol ester, which, in MeCN, was reacted with Et3N and Me2C(OH)CN to give I (R = O2N; R1, R3-R6 = H; R2 = Me; X = O) (II). II at 4.48 kg/ha in preemergent herbicidal test against foxtail, watergrass, velvetleaf, and Indian mustard, gave 100% control.

IT **114291-57-5P 114291-58-6P 114291-59-7P**
**114291-61-1P**
RL: AGR (Agricultural use); BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation); USES (Uses)

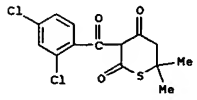
L8 ANSWER 14 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
(prepn. of, as herbicide)
RN 114291-57-5 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-(4-chloro-2-nitrobenzoyl)dihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



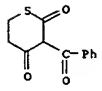
RN 114291-58-6 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-[2-chloro-4-(methylsulfonyl)benzoyl]dihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



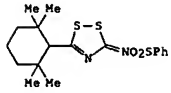
RN 114291-59-7 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-(2,4-dichlorobenzoyl)dihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



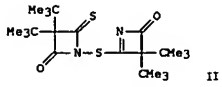
RN 114291-61-1 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-benzoyldihydro- (9CI) (CA INDEX NAME)



L8 ANSWER 15 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1988:186455 CAPLUS
DOCUMENT NUMBER: 108:186455
TITLE: Cycloaddition reactions of heterocumulenes. XXIX. Reactions of thioketenes with isocyanates
AUTHOR(S): Schaumann, Ernst; Moeller, Marianne; Adiwidjaja, Gunadi
CORPORATE SOURCE: Inst. Org. Chem., Univ. Hamburg, Hamburg, D-2000/13, Fed. Rep. Ger.
SOURCE: Chemische Berichte (1988), 121(4), 689-99
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 108:186455
GI

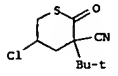


I



II

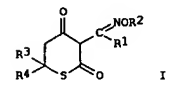
AB The [2+2] cycloaddn. of thioketenes to isocyanates gave as main products, 4-thioxo-2-azetidinones, which may isomerize to 4-imino-2-thietanones. In competing reactions, 2,4-azetidinediones, N-sulfonylamides, and 3H-1,2,4-dithiazoles are formed. Thioketenes reacted with chlorosulfonyl isocyanate to give N-unsubstituted 4-thioxo-2-azetidinones. Depending on the thioketene and the reaction conditions, other compds. also result. The structures of products I and II were determined by x-ray anal.
IT 112222-36-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 112222-36-3 CAPLUS
CN 2H-Thiopyran-3-carbonitrile, 5-chloro-3-(1,1-dimethylethyl)tetrahydro-2-oxo- (9CI) (CA INDEX NAME)



L8 ANSWER 16 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1986:442651 CAPLUS
DOCUMENT NUMBER: 105:42651
TITLE: Substituted tetrahydrothiopyran-2,4-diones
INVENTOR(S): Wroblowsky, Heinz Juergen; Stetter, Joerg; Eue, Ludwig; Schmidt, Robert R.; Santel, Hans Joachim
PATENT ASSIGNEE(S): Bayer A.-G., Fed. Rep. Ger.
SOURCE: Ger. Offen., 30 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| DE 3421351 | A1 | 19851212 | DE 1984-3421351 | 19840608 |
| US 4636245 | A | 19870113 | US 1985-737292 | 19850523 |
| EP 164056 | A2 | 19851211 | EP 1985-106547 | 19850529 |
| EP 164056 | A3 | 19861126 | | |
| EP 164056 | B1 | 19880907 | | |
| R: AT, BE, CH, DE, FR, GB, IT, LI, NL | | | | |
| AT 37027 | E | 19880915 | AT 1985-106547 | 19850529 |
| DK 8502551 | A | 19851209 | DK 1985-2551 | 19850606 |
| CA 1243324 | A1 | 19881018 | CA 1985-483300 | 19850606 |
| ZA 8504333 | A | 19860129 | ZA 1985-4333 | 19850607 |
| HU 38501 | A2 | 19860630 | HU 1985-2273 | 19850607 |
| JP 61007274 | A2 | 19860113 | JP 1985-123538 | 19850608 |

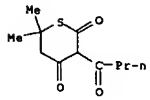
PRIORITY APPLN. INFO.: DE 1984-3421351 A 19840608
EP 1985-106547 A 19850529
OTHER SOURCE(S): CASREACT 105:42651
GI



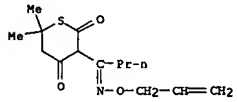
I

AB The title compds. [I; R1 = H, aliphatic, alkyl, alkoxy-, alkylthio-, halo-, cycloalkyl, (un)substituted aryl; R2 = aliphatic, alkyl, alkoxy-, alkylthio-, halo-, alkoxycarbonyl-, alkoxyiminoalkyl, haloalkenyl, (un)substituted aralkyl or heterocyclylalkyl; R3, R4 = H, alkyl, alkoxy-, alkylthio-, cycloalkyl, (un)substituted aryl, aryloxyalkyl, or aralkyl] and their metal salts, useful as herbicides (no data), were prepared 6,6-Dimethyltetrahydrothiopyran-2,4-dione in pyridine was treated with ZnCl2, then dropwise with PrCOCl to give 36.6% 6,6-dimethyl-3-butyryltetrahydrothiopyran-2,4-dione which was oximated with H2C:CHCH2ONH2.HCl in MeOH containing NaOMe to give 80% I (R1 = Pr, R2 = allyl, R3 = R4 = Me).
IT 102994-41-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and oximation of)
RN 102994-41-2 CAPLUS

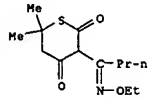
L8 ANSWER 16 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
CN 2H-Thiopyran-2,4(3H)-dione, dihydro-6,6-dimethyl-3-(1-oxobutyl)- (9CI) (CA INDEX NAME)



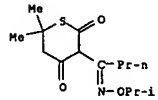
IT 102994-40-1P 102994-43-4P 102994-44-5P
RL: AGR (Agricultural use); BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation); USES (Uses)
(preparation of, as herbicide)
RN 102994-40-1 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, dihydro-6,6-dimethyl-3-[1-[(2-propenyloxy)imino]butyl]- (9CI) (CA INDEX NAME)



RN 102994-43-4 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, 3-[1-(ethoxyimino)butyl]dihydro-6,6-dimethyl- (9CI) (CA INDEX NAME)



RN 102994-44-5 CAPLUS
CN 2H-Thiopyran-2,4(3H)-dione, dihydro-6,6-dimethyl-3-[1-[(1-methylethoxy)imino]butyl]- (9CI) (CA INDEX NAME)

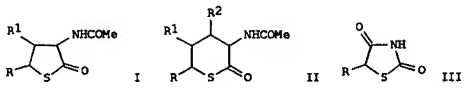


L8 ANSWER 16 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

L8 ANSWER 17 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1982:572413 CAPLUS
DOCUMENT NUMBER: 97:172413
TITLE: Silver dye-bleach preparation for a photographic silver dye-bleach process and bath
INVENTOR(S): Gerhardt, Wolfgang; Schneider, Werner
PATENT ASSIGNEE(S): Tetenal Photowerk G.m.b.H. und Co., Fed. Rep. Ger.
SOURCE: Ger. Offen., 19 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

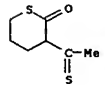
| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| DE 3045059 | A1 | 19811203 | DE 1980-3045059 | 19801129 |
| DE 3045059 | C2 | 19830623 | | |
| AT 8001877 | A | 19820315 | AT 1980-1877 | 19800404 |
| AT 368816 | B | 19821110 | | |

PRIORITY APPLN. INFO.: AT 1980-1877 A 19800404
GI




AB S-containing helerocyclic compds. of the formulas I, II, and/or III (R = H, Me, Et, SO3Na, Cl, NHCOMe; R1 = H, Me, Et, CO2H, Cl, NHCOMe; R2 = H, Me, Et, CO2H, SO3Na, p-NaO3SE6H4), which have no odor, are described for use as antioxidants in Ag-dye bleach process compns. These compds. are used at 0.0005-0.1 mol/L. Thus, to a Ag-dye bleach bath containing water 700 mL, sulfamic acid 140, Na 3-nitrobenzenesulfonate 5, 2,3-dimethylquinoxaline 1.3, KI 6.4 g, methylcellosolve 50 mL and water to 1 L was added a solution of 5-N-acetylamino-2,4-thiazolidinedione 0.5 g in water 100 mL. The resulting processing solution had no smell, liberated no I2 even after 8 mo, and yielded pos. photog. results.
IT **81515-92-6D**, derivs.
RL: USES (Uses)
(antioxidant, in silver dye-bleach photog. processing solns.)
RN 81515-92-6 CAPLUS
CN Acetamide, N-(tetrahydro-2-oxo-2H-thiopyran-3-yl)- (9CI) (CA INDEX NAME)

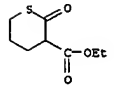

L8 ANSWER 18 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1970:42699 CAPLUS
DOCUMENT NUMBER: 72:42699
TITLE: Enethiols. V. Syntheses of α-thioacyl lactones and α-thioacyl thiollactospectroscopy
AUTHOR(S): Duus, Fritz; Pedersen, E. B.; Lawesson, Sven Olov
CORPORATE SOURCE: Dep. Org. Chem., Univ. Aarhus, Aarhus, Den.
SOURCE: Tetrahedron (1969), 25(23), 5703-20
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 72:42699
AB α-Thioacyl lactones and α-thioacyl thiol lactones were prepared in moderate to good yields by the action of H2S and HCl on the α-acyl-analogs. NMR and IR studies show that the aliphatic thioacyl compds. exist as equilibrium mixts. of the cis and trans-enethiol forms, whereas the thioaroyl-l actones are present exclusively as intramol. H-bonded cis-enethiols. The NMR spectra are discussed and the influence of different solvents on chemical shifts and coupling consts. are also described and discussed. The syntheses and properties of some methylated and acetylated α-thioacyl lactones are presented, and their absolute configurations determined by NMR spectroscopy.
IT **26792-34-7P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 26792-34-7 CAPLUS
CN 2H-Thiopyran-2-one, tetrahydro-3-(thioacetyl)- (8CI) (CA INDEX NAME)




L8 ANSWER 19 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1966:3700 CAPLUS
DOCUMENT NUMBER: 64:3700
ORIGINAL REFERENCE NO.: 64:603f-g
TITLE: α-Acylated δ-mercaptolactones
INVENTOR(S): Wiese, Friedrich F.; Korte, Friedhelm
PATENT ASSIGNEE(S): Shell Internationale Research Maatschappij N. V.
SOURCE: 2 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| DE 1201850 | | 19650930 | DE | 19630504 |

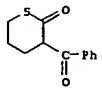
AB The title compds. are prepared by treating the esters of α-acylated δ-acetylthiovaleric acids in organic solvents with (EtO)2Mg at 100-200°. Thus, a mixture of 30 g. α-carbethoxy-δ-acetylthiovaleric acid ethyl ester, and 12 g. (EtO)2Mg in 100 ml. anhydrous xylene was refluxed and the condenser kept at 90° so that 15 ml. AcOEt was distilled The mixture was cooled, diluted with 300 ml. Et2O, and extracted with 2N HCl. The organic phase was evaporated in vacuo to obtain 15.5 g. α-carbethoxy-δ-mercaptovalerolactone, b0.05 85°, n20D 1.5070. α-Acylated δ-mercaptovalerolactones similarly prepared were: (substituent, n20D, and % yield given) acetyl, 1.5220, 84; benzoyl, -- [m. 110° (MeOH)], 73.5; the α-phosphonic acid diethyl ester δ-thiovalerolactone, b0.05 95-105°, n20D 1.5020, was prepared in 56% yield from α-carbethoxy-δ-acetylthiobutylphosphonic acid diethyl ester.
IT **4547-45-9**, Malonic acid, (3-mercaptopropyl)-, δ-(thio lactone), Et ester **4547-46-0**, Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) **4553-38-2**, Valeric acid, 2-benzoyl-5-mercapto-, δ-(thio lactone)
(preparation of)
RN 4547-45-9 CAPLUS
CN Malonic acid, (3-mercaptopropyl)-, δ-(thiolactone), ethyl ester (7CI, 8CI) (CA INDEX NAME)




RN 4547-46-0 CAPLUS
CN Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (6CI, 7CI, 8CI) (CA INDEX NAME)

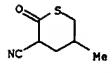

RN 4553-38-2 CAPLUS

L8 ANSWER 19 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
CN Valeric acid, 2-benzoyl-5-mercapto-, δ-(thiolactone) (7CI, 8CI) (CA INDEX NAME)



L8 ANSWER 20 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1964:447451 CAPLUS
DOCUMENT NUMBER: 61:47451
ORIGINAL REFERENCE NO.: 61:8185b-h,8186a-c
TITLE: Acyllactone rearrangement. XXXI. Syntheses of α-cyanolactams, α-cyano-γ- and δ-thiollactones and their behavior under the conditions of the acyllactone rearrangement
AUTHOR(S): Korte, Friedhelm; Wamhoff, Heinrich
SOURCE: Ber. (1964), 97(7), 1970-80
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 61:47451
GI For diagram(s), see printed CA Issue.
AB α-Cyano-γ- and δ-lactams and thiollactones were prepared The lactams were not rearranged by acids or bases but the thiollactones gave under these conditions dihydrothiophenes and dihydrothiopyrans, the structure of which was proved by their reactions and infrared spectra. MeCH(CN)CO2Et with Br(CH2)3Cl by the method of Gagnon, et al. (CA 44, 9352a) yielded Cl(CH2)3CMe(CN)CO2Et (I), b0.1 71°. ClCH2CH2CMe(CN)CO2Et (II), b8 125-7°, was prepared similarly from ClCH2CH2Br. Cl(CH2)3CH(CN)CO2Et (III) (112 g.) shaken with 135 cc. aqueous MeNH2 to solution and kept 1 hr. at room temperature gave 93 g. Cl(CH2)3CH(CN)CONHMe (IV), m. 75-6° (Me2CO-petr. ether). II (37.8 g.) gave similarly 17 g. Cl(CH2)2CMe(CN)CONHMe (V), m. 79°. II (37.8 g.) with NH4OH yielded 18 g. Cl(CH2)2CMe(CN)CONH2 (VI), m. 101°. I (40.7 g.) with MeNH2 gave 15.5 g. Cl(CH2)3CMe(CN)CONHMe (VII), m. 71°. I (40.7 g.) with NH4OH gave Cl(CH2)3CMe(CN)CONH2 (VIII), m. 94.5°. IV (69.6 g.) in 350 cc. absolute EtOH refluxed 1.5 hrs. with 9.2 g. Na in 250 cc. EtOH yielded 37 g. 1-methyl-3-cyano-2-piperidone (IX), pale yellow oil, b0.1 118-19°. IV (28 g.) gave similarly 9.5 g. 1-Me derivative of 3-methyl-3-cyano-2-pyrrolidone (X), b0.01 83.5°. VI (32 g.) gave 9.0 g. X, m. 103-5° (Me2CO). VII (36.1 g.) yielded 19.5 g. 3-Me derivative of IX, b0.05 84-5°. VIII (5.22 g.) gave 1.34 g. 3-methyl-3-cyano-2-piperidone, m. 119° (Me2CO). Fused 1-benzoyl-2-pyrrolidone (93 g.), 1 g. Bz2O2, and 159.8 g. Br irradiated with ultraviolet light and heated an addnl. 0.5 hr. yielded 92.4 g. 3,3-dibromo-2-pyrrolidone (XI), m. 165-6° (decomposition) (Me2CO). XI (24.3 g.) hydrogenated 12 min. yielded 8.3 g. 3-bromo-2-pyrrolidone (XII), leaflets, m. 83°. 3,3-Dibromo-2-piperidone (38.5 g.) gave similarly 16.6 g. 3-bromo-2-piperidone (XIII), leaflets, m. 114-16° (Me2CO). XII (32.8 g.) and 10.0 g. NaCN in 200 cc. 96% EtOH refluxed 20 hrs. with stirring yielded 15.4 g. 3-cyano-2-pyrrolidone, m. 78-9° (Me2CO). XIII (35.6 g.) gave similarly 13.0 g. 3-cyano-2-piperidone, m. 68-70°. α-Bromo-ε-caprolactam (34.8 g.) yielded similarly 17.5 g. α-CN analog, m. 92-6°. IX (10 g.) in 50 cc. 4% alc. HCl refluxed 15 hrs. yielded 9.0 g. 1-methyl-3-carbethoxy-2-piperidone (XIV), b0.05 82°. IX (13.8 g.) in 150 cc. MeOH and 5 g. Raney Ni hydrogenated 17 hrs. at room temperature and 115 atmospheric yielded 5.6 g. 3-H2NCH2 analog of XIV, b0.01 65-7°. IX (6.9 g.) in 50 cc. concentrated HCl or 50 cc. concentrated NH4OH kept 48 hrs. at room temperature yielded 7.3 g. 3-CONH2 analog of XIV, m. 132-5° (EtOH). IX (27.6 g.) and 20 millimoles EtONa in absolute EtOH heated at 250° in an autoclave during 25 hrs. gave polymerization products and 7.8 g. 1-methyl-2-piperidone. IX (6.9 g.) added to 1.2 g. Na in 25 cc. absolute EtOH yielded the 3-Na derivative (XV) of IX. IX (13.8 g.) added to 2.4 g. Na in 200 cc. absolute EtOH and

L8 ANSWER 20 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
refluxed with 17 g. EtI yielded 13 g. 1-methyl-3-ethyl-3-cyano-2-piperidone (XVI), b0.01 98-100°. XV (18.7 g.) in 200 cc. C6H6 with 8.6 g. AcCl yielded 7.5 g. 3-Ac analog of XVI, b0.05 104°. IX (41.4 g.) in 13.8 g. abs. EtOH treated with cooling with 12.4 g. dry HCl and added after 3-4 hrs. to 33% aq. K2CO3 yielded 32.5 g. 3-aminoethoxymethylene analog (XVII) of XIV, b0.05 83-8°. XVII (25.4 g.) and 100 cc. 3N KOH stirred 70 hrs. at room temp. yielded 12 g. 3-CO2H analog of XIV, m. 119°. XVII (9.1 g.) treated 3 days at room temp. with 4% alc. HCl yielded 3.2 g. XIV. XVII (9.2 g.) refluxed 18 hrs. with 0.12 g. Na in 50 cc. abs. EtOH and neutralized with 3 g. AcOH yielded IX. II (159 g.) added dropwise at 70° to 19.4 g. Na in 1 l. abs. EtOH and 64 g. AcSH yielded 135 g. yellow, oily AcS(CH2)2CMe(CN)CO2Et (XVIII), b0.01 98°. CH2:CHCH2CH(CN)CO2Et (153 g.), a small amt. Bz2O2, and 76 g. AcSH heated 3 hrs. at 80° yielded 93 g. yellow, oily AcS(CH2)3CH(CN)CO2Et (XIX), b0.05 116.5°. III (189 g.) and 1.00 mole AcSNa gave similarly 264 g. XIX. I (103 g.) with AcSH yielded 89 g. AcSCH2CHMeCH2CH(CN)CO2Et (XX), b0.05 117-19°. XVIII (115 g.) in 500 cc. dry xylene refluxed with 65 g. (EtO)2Mg with the removal of AcOEt gave 23 g. yellow, oily α-methyl-α-cyano-γ-thiolbutyrolactone (XXI), b0.05 61°. XIX (114.5 g.) gave similarly 48 g. α-cyano-δ-thiolvalerolactone (XXII), b0.01 90°. XX (72 g.) gave 38.5 g. γ-methyl-α-cyano-δ-thiolvalerolactone (XXIII). AcSCH2CH2Br (130 g.) added dropwise to 23 g. Na in 1 l. abs. EtOH and 120 g. NCCH2CO2Et yielded 20.0 g. 2-amino-3-carbethoxy-4,5-dihydrothiophene (XXIV), pale yellow crystals, m. 78° (Me2CO-petr. ether). XXIV (20.14 mg.) in 1 cc. 0.17N HCl in CHCl3 yielded XXV. XXI (7.1 g.) refluxed 19 hrs. with 115 mg. Na in 40 cc. abs. EtOH and neutralized with 0.3 AcOH yielded 5.2 g. 2-imino-3-methyl 3-carbomethoxytetrahydrothiophene , b0.01 59°, which was also obtained similarly in 75% yield during 24 hrs. from 22.9 g. XVIII. XXII (14.2 g.) refluxed 18 hrs. gave 15.7 g. 2-amino-3-carbethoxy-5,6-dihydro-4H-thiopyran (XXVI), pale yellow plates, m. 58° (Me2CO-petr. ether). XIX refluxed 26 hrs. gave 18.1 g. XXVI. XXII (28.4 g.) treated with 9.2 g. EtOH and 7.3 g. HCl yielded 36.8 g. XXVI. XXVI (19.71 mg.) with 1 cc. 0.23N HCl in CHCl3 yielded XXVII (R = H). XXIII (15.5 g.) refluxed 22 hrs. gave crude 5-Me deriv. (XXVIII) of XXVI which was also obtained similarly from XX. XXVIII (19.87 mg.) in 1 cc. 0.13N HCl in CHCl3 gave XXVII (R = Me). XXIV with Ac2O gave the N-Ac deriv., m. 73-4°. XXVI (4.1 g.) gave similarly 3.3 g. N-Ac deriv., m. 103°. The ultraviolet and infrared absorption max. of the various new compds. are tabulated.
IT 91724-45-7, Valeric acid, 2-cyano-5-mercapto-4-methyl-, δ-(thio lactone) 93507-46-1, Valeric acid, 2-cyano-5-mercapto-, δ-(thio lactone) (preparation of)
RN 91724-45-7 CAPLUS
CN Valeric acid, 2-cyano-5-mercapto-4-methyl-, δ-(thiolactone) (7CI) (CA INDEX NAME)

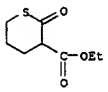


RN 93507-46-1 CAPLUS
CN Valeric acid, 2-cyano-5-mercapto-, δ-(thiolactone) (7CI) (CA INDEX NAME)

L8 ANSWER 20 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

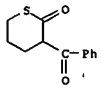
L8 ANSWER 21 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1964:447450 CAPLUS
DOCUMENT NUMBER: 61:47450
ORIGINAL REFERENCE NO.: 61:8184e-h,8185a-b
TITLE: Acyllactone rearrangement. XXX. Synthesis of α-acyl-δthiollactones and A2-dihydrothiopyrans
AUTHOR(S): Korte, Friedhelm; Wiese, Friedrich Franz
CORPORATE SOURCE: Univ. Bonn, Germany
SOURCE: Ber. (1964), 97(7), 1963-9
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 61:47450
GI For diagram(s), see printed CA Issue.
AB cf. CA 60, 3127b. δ-Acetylthio-α-acylvaleric acid esters were cyclized to α-acyl-δ-thiollactones (I) with the elimination of AcOEt. The preparation of II and of a series of I is described. A series of A2-dihydrothiopyrans was prepared readily by the protoncatalyzed alcoholysis of δ-acetylthio ketones. ClCH2CO2Et (270 g.) and 332 g. (EtO)3P heated 3 hrs. at 120-35° gave EtCl and 420 g. Et02CCH2P(O)(OEt)2 (III), b0.05 72-80°, n20D 1.4320. III (224 g.) and 168 g. CH2:CHCH2Br treated dropwise at 60° during 2 hrs. with 82 g. EtONa in 500 cc. absolute EtOH and refluxed 1 hr. yielded 223 g. CH2:CHCH2CH(CO2Et)P(O)(OEt)2 (IV), b0.05 95-110°, n20D 1.4490. IV (223 g.) treated with 0.5 g. Bz2O2 and 76 g. AcSH and kept 14 hrs. yielded 249 g. AcS(CH2)3CH(CO2Et)P(O)(OEt)2 (V), b0.05, 149-52°, n20D 1.4715. V (30.0 g. and 12.0 g. (EtO)2Mg in 150 cc. dry xylene refluxed 40 min. with the removal of about 15 cc. distillate yielded 12.5 g. II, b0.05 95-110°, n20D 1.5020. V (34 g.) in 150 cc. 5% alc. HCl refluxed 3 hrs. gave 26 g. HS(CH2)3CH(CO2Et)P(O)(OEt)2, b0.05 115-20°, n20D 1.4730. CH2:CHCH2CH(CO2Et)2 (165 g.), 1 g. Bz2O2, and 76 g. AcSH yielded 180 g. AcS(CH2)3CH(CO2Et)2 (VI), b0.05 112-14°, n20D 1.4685. VI (30 g.), 12 g. (EtO)2Mg, and 100 cc. dry xylene heated 0.5 hr. gave 15.5 g. VII (R = CO2Et), b0.05 85°, n20D 1.5070. CH:CHCH2CHAcCO2Et (170 g.), 1 g. Bz2O2, and 84 g. AcSH kept 14 hrs. gave 210 g. AcS(CH2)3CHAcCO2Et (VIII), b0.05 110-20°, n20D 1.4784. VIII (30.0 g.) with (EtO)2Mg in xylene gave 16.3 g. VII (R = Ac), b0.05 65-8°; it gives a blue FeCl3 reaction. CH2CHCH2CHBzCO2Et (116 g.), 1 g. Bz2O2, and 42 g. AcSH kept 14 hrs. yielded 111 g. AcS(CH2)3CHBzCO2Et (IX), b0.05 155°, n20D 1.5343. IX (20 g.) and 10 g. (EtO)2Mg refluxed in xylene, and the viscous, sirupy product treated with 20 cc. MeOH and kept 14 hrs. at 0° gave 10.5 g. VII (R = Bz), powder, m. 113-15°; it gives a blue-violet FeCl3 reaction after 2 hrs. standing. VIII (30 g.) in 300 cc. 10% alc. HCl refluxed 14 hrs. and concentrated in vacuo until the liquid turned turbid gave 18.5 g. X (R = Me), b0.05 69°, n20D 1.5350. IX (20 g.) refluxed 18 hrs. with 30 g. dry HCl in 350 cc. EtOH gave 13 g. X (R = Ph), b0.05 120°, n20D 1.5905; a 3-g. portion heated with 50% aqueous KOH gave 2 g. 3-CO2H analog, rods, m. 162° (ligroine). CH2:CHCH2CHAc2 (95 g.), 1 g. Bz2O2, and 60 g. AcSH yielded 128 g. AcS(CH2)3CHAc2 (XI), b0.05, 98-102°, n20D 1.4978. XI (21.6 g.) in 150 cc. EtOH, 50 cc. H2O, and 20 cc. concentrated HCl refluxed until a drop of the mixture no longer gave a violet color reaction with FeCl3 yielded 10.5 g. 2-methyl-3-acetyl-A2-dihydrothiopyran, b0.05 59°, n20D 1.5705; 2,4-dinitrophenylhydrazone m. 156° (MeOH); semicarbazone m. 212-13° (MeOH). CH2:CHCH2CH2Bz (40 g.), 0.5 g. Bz2O2, and 23 g. AcSH yielded 31 g. AcS(CH2)4Bz (XII), leaflets, m. 67-9° (ligroine). XII (30 g.) in 300 cc. EtOH and 20 cc. concentrated HCl refluxed 3 hrs. gave 19 g. 2-phenyl-A2-dihydrothiopyran, b0.05 82°, m. 36° (MeOH).

L8 ANSWER 21 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
IT 4547-45-9, Malonic acid, (3-mercaptopropyl)-, δ-(thio lactone), Et ester 4547-46-0, Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) 4553-38-2, Valeric acid, 2-benzoyl-5-mercapto-, δ-(thio lactone)
(preparation of)
RN 4547-45-9 CAPLUS
CN Malonic acid, (3-mercaptopropyl)-, δ-(thiolactone), ethyl ester (7CI, 8CI) (CA INDEX NAME)



RN 4547-46-0 CAPLUS
CN Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (6CI, 7CI, 8CI) (CA INDEX NAME)

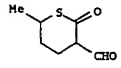
RN 4553-38-2 CAPLUS
CN Valeric acid, 2-benzoyl-5-mercapto-, δ-(thiolactone) (7CI, 8CI) (CA INDEX NAME)



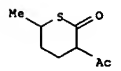
L8 ANSWER 22 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1963:37120 CAPLUS
DOCUMENT NUMBER: 58:37120
ORIGINAL REFERENCE NO.: 58:6333b
TITLE: Acyl lactone rearrangement. XXVI. The ultraviolet spectra of α-acyl lactones, α-acyl thiol lactones, and α-acyl lactams
AUTHOR(S): Buechel, Karl Heinz; Korte, Friedhelm
CORPORATE SOURCE: Univ. Bonn, Germany
SOURCE: Zeitschrift fuer Analytische Chemie (1962), 190, 243-50
CODEN: ZANCA8; ISSN: 0372-7920
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. CA 58, 5733c. The wavelength and extinction coefficient in the ultraviolet are given for 26 α-acyl δ-lactones, 21 α-acyl γ-lactones, 9 α-acyl γ-and δ-thiol lactones, 14 α-acyl γ-lactams, and 8 α-acyl δ-lactams.
IT 4547-46-0, Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) 89533-72-2, Malonaldehydic acid, (3-mercaptopropyl)-, δ-(thio lactone) 89898-13-5, Malonaldehydic acid, (3-mercaptobutyl)-, δ-(thio lactone) 90482-26-1, Hexanoic acid, 2-acetyl-5-mercapto-, δ-(thio lactone) 92474-87-8, Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), Et ester 95141-96-1, Oxalacetic acid, (3-mercaptobutyl)-, δ-(thio lactone), Et ester
(preparation of)
RN 4547-46-0 CAPLUS
CN Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (6CI, 7CI, 8CI) (CA INDEX NAME)

RN 89533-72-2 CAPLUS
CN Malonaldehydic acid, (3-mercaptopropyl)-, δ-(thio lactone) (7CI) (CA INDEX NAME)

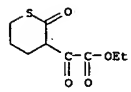
RN 89898-13-5 CAPLUS
CN Malonaldehydic acid, (3-mercaptobutyl)-, δ-(thio lactone) (7CI) (CA INDEX NAME)



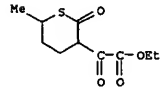
L8 ANSWER 22 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
RN 90482-26-1 CAPLUS
CN Hexanoic acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (7CI) (CA INDEX NAME)



RN 92474-87-8 CAPLUS
CN Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), ethyl ester (7CI) (CA INDEX NAME)



RN 95141-96-1 CAPLUS
CN Oxalacetic acid, (3-mercaptobutyl)-, δ-(thiolactone), ethyl ester (7CI) (CA INDEX NAME)



L8 ANSWER 23 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1962:38437 CAPLUS
DOCUMENT NUMBER: 56:38437
ORIGINAL REFERENCE NO.: 56:7282c-g
TITLE: 4,5-Dihydrothiophene- and 5,6-dihydrothiapyran-3-carboxylic acid esters
INVENTOR(S): Korte, Friedhelm; Loehmer, Karl H.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|---|---|---|---|
| DE 1107241 | | 19570129 | DE | |

OTHER SOURCE(S): CASREACT 56:38437

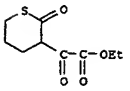
AB γ- or δ-Thiolactones were condensed with Me or Et carboxylates in the presence of basic condensation agents (except alkali metal alcoholates) and the formed α-acyl-γ-(or δ)-thiolactones were treated with alcs. in the presence of acidic catalysts to give the title compds., useful as intermediates for pharmaceuticals, disinfectants, and pesticides. Thus, to 12.6 g. Mg (chips) in 100 ml. Et2O was added 56.7 g. EtBr in 80 ml. Et2O, and, after dissolution, 52 g. isoPr2NH in 100 ml. Et2O and then 51 g. γ-thiobutyrolactone and 49 g. HCO2Et in 150 ml. Et2O were added dropwise at 35° and the mixture was stirred overnight at 35°. Then 300 ml. concentrated HCl and ice was added, the ether layer separated, the aqueous phase extracted with Et2O, the combined ether solns. dried (CaCl2), the ether removed, and the residue fractionated at 73-80°/0.3 mm. to give 11 g. α-formyl-γ-thiobutyrolactone, m. 72-4°. The product (11 g.) in 150 ml. 4% HCl-MeOH was refluxed 48 hrs., the HCl-MeOH removed in vacuo at 40°, the residue taken up in 150 ml. Et2O, the ether solution washed with 20 ml. aqueous NaHCO3, dried (Na2SO4), the ether removed, and the residue fractionated at 43-46°/0.5 mm. to give 10 g. 3-carbomethoxy-4,5-dihydrothiophene (oil). Similarly were made: α-ethoxalyl-γ-thiobutyrolactone (oil) and 2,3-dicarbethoxy-4,5-dihydrothiophene (oil); αacetyl-γ-thiobutyrolactone, b0.05 60°, and 2-methyl-3-carbomethoxy-4,5-dihydrothiophene, b0.5 52-4°; α-formyl-δ-thiovalerolactone, m. 60-2°, and 3-carbomethoxy-5,6-dihydrothiopyran, b0.16 64-6°; α-acetyl-δ-thiovalerolactone, b0.15 85-6°, and 3-carbomethoxy-2-methyl-5,6-dihydrothiopyran, b0.4 65-7°; α-ethoxalyl-δ-thiovalerolactone, b0.2 115-17°, and 2,3-dicarbethoxy-5,6-dihydrothiopyran, b0.3 119-20°.

IT **4547-46-0**, Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) **89533-72-2**, Malonaldehydic acid, (3-mercaptopropyl)-, δ-(thio lactone) **92474-87-8**, Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), Et ester
(preparation of)

RN 4547-46-0 CAPLUS
CN Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (6CI, 7CI, 8CI) (CA INDEX NAME)

L8 ANSWER 23 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
RN 89533-72-2 CAPLUS
CN Malonaldehydic acid, (3-mercaptopropyl)-, δ-(thio lactone) (7CI) (CA INDEX NAME)

RN 92474-87-8 CAPLUS
CN Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), ethyl ester (7CI) (CA INDEX NAME)

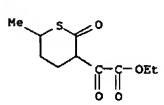


L8 ANSWER 24 OF 25 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1961:137443 CAPLUS
DOCUMENT NUMBER: 55:137443
ORIGINAL REFERENCE NO.: 55:25923b-i,25924a-e
TITLE: Acyl-lactone rearrangement. XVII. Synthesis of γ- and δ-thiollactones and the mechanism of their ring cleavage
AUTHOR(S): Korte, Friedhelm; Christoph, Helmut
CORPORATE SOURCE: Univ. Bonn, Germany
SOURCE: Chemische Berichte (1961), 94, 1966-76
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 55:137443
GI For diagram(s), see printed CA Issue.

AB Alkyl- substituted γ- and δ-lactones were synthesized. α-Acyl-δ-thiolcaprolactones rearranged to the 6-methyl-5,6-dihydro-4H-thiopyrans. The ring stabilization by alkyl-substitution was demonstrated by measuring the acidic and alkaline hydrolysis rates; the ring opening occurred in all cases by acyl-cleavage. Me2C:CH(CH2)2CO2H (40 g.) and 28 g. AcSH heated 24 hrs. on the water bath yielded 65% Me2CHCH(SAc)(CH2)2CO2H (I), b0.1 112-14°. I (30 g.) and 30 g. NaOH in 250 cc. H2O kept overnight, acidified with 6N HCl, and extracted with Et2O yielded 20 g. Me2CHCH(SH)(CH2)2CO2H (II), b10135°. II (20 g.) heated 0.5 hr. at 260° gave 15 g. γ-isopropyl-γ-thiobutyrolactone, b12 105°. BrCH2CMe:CMe2 (320 g.) in 200 cc. EtOH added dropwise to 46 g. Na and 320 g. CH2(CO2Et)2 in 500 cc. EtOH at 95-100°, the mixture heated several hrs. with stirring, cooled, filtered, and distilled yielded 300 g. Me2C:CMeCH2CH(CO2Et)2 (III), b15 140°. III (300 g.), 200 g. KOH, and 600 cc. H2O refluxed 3 hrs. with stirring with removal of the EtOH, acidified with 6N HCl, and the product heated 3 hrs. at 180-200° yielded 128 g. Me2C:CMeCH2CH2CO2H (IV), b0.6 80-2°. IV (105 g.) and 90 g. AcSH heated 24 hrs. on the water bath gave 55% mixture of Me2C(SAc)CHMe(CH2)2CO2H (V) and Me2CHCMe(SAc)(CH2)2CO2H (VI), yellowish oil, b0.1 125-45°. V-VI mixture (40 g.), 40 g. NaOH, and 400 g. H2O kept 2 days, acidified with HCl, and extracted with Et2O yielded Me2CHCMe(SH)(CH2)2CO2H (VII), b14 120-30°, and 84% Me2C(SH)CHMe(CH2)2CO2H (VIII), b14 155°. VIII (12 g.) heated 1 hr. at 120° yielded 90% γ,δ-dimethyl-δ-thiolcaprolactone (IX), b10 120°. VII (15 g.) gave similarly 92% γ-methyl-γ-isopropyl-γ-thiolbutyrolactone (X), b12 110°. IV (100 g.) in 200 cc. petr. ether (b. 40-60°) and 200 g. SOCl2 heated several hrs. on the steam bath gave 91 g. acid chloride (XI) of IX, b14 79°. XI (90 g.) added slowly dropwise with cooling to 400 cc. dry C5H5N (saturated with dry H2S) while treating with dry H2S, the mixture acidified with 5N HCl, and extracted with Et2O yielded 72% Me2C:CMe(CH2)2COSH (XII), b16 106°. In the same manner were prepared the following acids (b.p./mm. and % yield given): Me2C:CH(CH2)2COSH (XIII), 93°/16, 53; Me2C:CHCH2COSH (XIV), 85°/12, 40; CH2:CH(CH2)2COSH (XV), 61°/18, 54; CH2:CH(CH2)3COSH (XVI), 66°/10, 50; CH2:CH(CH2)4COSH (XVII), 90-2°/16, 60. XII spontaneously evolved X, b0.6 70°. XIII yielded similarly γ-isopropyl-γ-thiolbutyrolactone (XVIII), b12 98°. XIV gave in the same manner γ,γ-dimethyl-γ-thiolbutyrolactone (XIX), b12 103°. XV gave similarly 45% γ-methyl-γ-thiolbutyrolactone (XX), b18 90°, and 50% [(CH2)4COS]x, powder, m. 115-17° (C6H6), mol. weight 1020, which were separated by trituration with MeOH. XVI gave 92% polythioester, m. 80-2°, mol. weight 2140, and XVII yielded polythioester, m. 69°, mol. weight 1620. Ac(CH2)3CO2Na (85 g.) in 500 cc. H2O and 50 g. S hydrogenated 8 hrs. at 175°/100 atmospheric over 15 g. Raney Ni, filtered, acidified with concd. HCl, and extd. with EtOAc yielded 58 g. MeCH(SH)(CH2)3CO2H (XXI), b0.8 100-5°. XXI (23 g.) heated 1 hr. at 250° yielded 18 g. δ-thiolcaprolactone (XXII), b13 110°. EtMgBr from 6 g. Mg and 24 g. EtBr in 100 cc. abs. Et2O treated dropwise with stirring with 23 g. iso-Pr2NH in 150 cc. dry Et2O at 35°, the mixt. cooled, treated dropwise with 26 g. XXII and 23.7 g. HCO2Et in 75 cc. Et2O, stirred 6 hrs., acidified with cooling with dil. HCl, and extd. with Et2O yielded 10.5 g. α-hydroxymethylene deriv. (XXIII), m. 65°, b0.5 80-1°, violet with FeCl3. XXIII (10 g.) in 150 cc. abs. MeOH contg. 6% HCl refluxed 24 hrs., evapd., the residue dissolved in Et2O, neutralized with aq. NaHCO3, and worked up gave 8.6 g. 6-methyl-3-carbomethoxy-5,6-dihydro-4H-thiopyran (XXIV), b0.2 63°. XXIV (2 g.) shaken to soln. with 2 g. KOH in 40 cc. H2O and acidified with cooling with 6N HCl yielded 92% 6-methyl-5,6-dihydro-4H-thiopyran-3-carboxylic acid (XXV), m. 96° (petr. ether). IsoPr2NMgBr from 23 g. iso-Pr2NH treated dropwise with 26 g. XXII and 36 g. EtOAc in 100 cc. Et2O, the mixt. stirred 8 hrs., and acidified with cold dil. HCl gave 30% α-Ac deriv. (XXVI) of XXII, b0.6 88-90°. XXVI (5 g.) and 150 cc. abs. MeOH contg. 10% HCl refluxed 20 hrs. yielded 4.1 g. 2-Me deriv. (XVII) of XXIV, b0.01 58°. XXVII (2 g.) and 2 g. KOH in 40 cc. H2O shaken to soln., acidified with cooling, and filtered gave 92% 2-Me deriv. of XXV, m. 65° (H2O). XXII (24 g.) and 29 g. (CO2Et)2 condensed in the usual manner in iso-Pr2NMgBr in Et2O, stirred 5 hrs., kept overnight, acidified with 2N HCl, and extd. with Et2O yielded 72% α-EtO2CCO deriv. (XXVIII) of XXII, yellow oil, b. 90-2° (in vacuo), blue with FeCl3. XXVIII (12 g.) in 150 cc. 10% abs. alc. HCl refluxed 24 hrs. yielded 81% 6-methyl-2,3-dicarbethoxy-5,6-dihydro-4H-thiopyran, b0.1 103°. γ-Thiolbutyrolactone (XXIX) (5 g.) and 25 cc. 5N HCl heated 2 hrs. with a small amt. of MeOH and the mixt. extd. with Et2O gave 75% HS(CH2)3CO2H (XXX), b12 132°. XXII (2 g.) in 30 cc. 5N HCl shaken with warming 2 hrs. and extd. with Et2O yielded 80% XXI, b15 140°. IX (2 g.) shaken with warming with 30 cc. 5N HCl, kept 24 hrs., and extd. with Et2O gave 90% VIII, b10 145°. X (15 g.) in 50 cc. MeOH shaken 0.5 hr. with 16 g. NaOH in 500 cc. H2O, acidified with H2SO4, and extd. with Et2O gave 87% VII, rhombs, m. 51° (petr. ether). XXIX (6 g.) in 10 cc. MeOH and 20 cc. N NaOH kept 2 hrs., acidified, and extd. with Et2O yielded 98% XXX, b11 140°. The rate of the ring opening was measured by ultraviolet spectroscopy; the appropriate thiolactone (0.1 g.) in 5 cc. MeOH was treated with 20 cc. N or 5N HCl and heated 2 hrs. under a stream of N (thiolactone used and % yields of mercapto deriv. and unchanged thiolactone obtained with N HCl and with 5N HCl catalyst given in this order): XXIX, 62, 38, 78, 21; XX, 42, 58, 53, 46; XVIII, 24, 75, 28, 70; X, 2, 98, 5, 95; XIX, 20, 80, 30, 70; XXII, 100, 0, 100, 0; δ-Me deriv. of XXII, 78, 20, 95, 5; IX, 80, 18, 92, 6.

IT **95141-96-1**, Oxalacetic acid, (3-mercaptobutyl)-, δ-(thio lactone), Et ester
(preparation of)

RN 95141-96-1 CAPLUS
CN Oxalacetic acid, (3-mercaptobutyl)-, δ-(thiolactone), ethyl ester (7CI) (CA INDEX NAME)



ACCESSION NUMBER: 1960:97559 CAPLUS
DOCUMENT NUMBER: 54:97559
ORIGINAL REFERENCE NO.: 54:18496a-g
TITLE: Acyl-lactone rearrangement. XIII. The synthesis of dihydrothiopyran- and dihydrothiophene-3-carboxylic acid
AUTHOR(S): Korte, Friedhelm; Buchel, Karl Heinz
CORPORATE SOURCE: Univ. Bonn, Germany
SOURCE: Chemische Berichte (1960), 93, 1021-5
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 54:97559

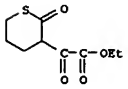
AB cf. CA 54, 5692h. α-Acyl-δ-thiollactones rearranged in aqueous HCl to dihydrothiopyran-3 carboxylic acids. The similar rearrangement of α-acyl-γ-thiollactones succeeded only partially and was dependent on the acyl substituents. HS(CH2)4CO2H (142 g.), prepared by the method previously described (CA 53, 1321b), distilled slowly at 270°, and the orange distillate dissolved in Et2O, washed, dried, and fractionated gave 81 g. δ-thiolvalerolactone (I), b0.6 63-6°. Iso-Pr2NH (42 g.) in 100 cc. Et2O added dropwise with stirring to EtMgBr from 10.1 g. Mg and 46 g. EtBr, the mixture cooled below -10°, treated with 34.8 g. I and 40 g. (CO2Et)2 (II) in 120 cc. absolute Et2O dropwise below 5°, stirred 12 hrs. at room temperature, treated with stirring with ice and dilute HCl, and the product isolated with Et2O gave 47.9 g. α-EtO2CCO derivative (III) of I, b0.1 113-15°; it gave a wine-red color with FeCl3 in aqueous MeOH. I, HCO2Et, and EtMgBr in the ratio 1:1:1.4 processed in the usual manner, the crude product distilled, and the fraction b0.5 70-90° refrigerated 8 days yielded 11.5 g. α-HOCH2 derivative (IV) of I, m. 60-2°; it gave a violet color with FeCl3. I, EtOAc, and EtMgBr yielded similarly 25% α-Ac derivative (V) of I, b0.05 79-83°; it gave a blue color with FeCl3; a higher boiling fraction, b0.05 108-14°, yielded a red color with FeCl3. IV (10 g.) in 40 cc. concentrated HCl kept 12 hrs. and filtered gave 3.3 g. 5,6-dihydro-4H-thiopyran-3-carboxylic acid (VI), m. 93-4° (sublimed). V (10 g.) in 40 cc. concentrated HCl kept 1 hr. at 0°, diluted with 40 cc. H2O, and filtered yielded 8.9 g. 2-Me derivative of VI, m. 130° (sublimed). III (10 g.) in 60 cc. concentrated HCl refrigerated 48 hrs. and filtered gave 6.5 g. 5,6 dihydro-4H-thiopyran-2,3-dicarboxylic anhydride, light yellow, m. 42-3°. CH2:CHCH2CO2H (110 g.), b12 69-70°, treated dropwise with stirring with 121 g. AcSH, b. 88-94°, warmed to 80°, kept at room temperature overnight, and distilled gave 191 g. adduct, b3 138-9°, which, cyclized in the usual manner, gave 93 g. δ-thiolbutyrolactone (VII), b3.5 55-6°. VII condensed with II in the usual manner yielded 65% α-EtO2CCO derivative (VIII) of VII, yellow oil, b0.05 111-14°; it gave a red-violet color with FeCl3. VII condensed in the usual manner with HCO2Et yielded 26% α-HOCH2 derivative (IX) of VII, m. 69-74°; it gave a blue-violet color with FeCl3. VII (30.6 g.) and 35.2 g. EtOAc gave 11.2 g. α-Ac derivative (X) of VII; it gave a blue-violet color with FeCl3; the higher boiling fractions and the residue combined and recrystd. from boiling MeOH gave 1.8 g. dithiobutyrolactone, m. 92°. VIII (10 g.) in 50 cc. concentrated HCl kept 5 days at room temperature and filtered gave 8.2 g. 4,5-dihydrothiophene-2,3-dicarboxylic acid, yellow prisms, m. 196-8°. IX (1 g.) in 10 cc. concentrated HCl stirred to solution, kept 4 days, and filtered deposited 100 mg. 4,5-dihydrothiophene-3-carboxylic acid (XI), m. 155-9°. A similar run with 1:1 concentrated HCl-EtOH gave 200 mg. XI. X (3 g.) in 12 cc. concentrated HCl refrigerated 8 days and filtered yielded 0.1 g. 3-Me deriv. of XI.



IT 4547-46-0, Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) 92474-87-8, Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), Et ester
(preparation of)

RN 4547-46-0 CAPLUS
CN Valeric acid, 2-acetyl-5-mercapto-, δ-(thio lactone) (6CI, 7CI, 8CI) (CA INDEX NAME)


RN 92474-87-8 CAPLUS
CN Oxalacetic acid, (3-mercaptopropyl)-, δ-(thio lactone), ethyl ester (7CI) (CA INDEX NAME)



=> log y

| COST IN U.S. DOLLARS | SINCE FILE ENTRY | TOTAL SESSION |
|---|---|---|
| FULL ESTIMATED COST | 123.95 | 447.70 |

| DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS) | SINCE FILE ENTRY | TOTAL SESSION |
|---|---|---|
| CA SUBSCRIBER PRICE | -18.25 | -18.25 |

STN INTERNATIONAL LOGOFF AT 15:48:16 ON 16 MAY 2005